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REVIEW ARTICLE

Vibrational spectroscopic approaches to conformational equilibria and kinetics (in condensed media)

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1. INTRODUCTION

TO INTERPRET a wide variety of phenomena in statistical thermodynamics, and when considering mechanisms and rates of chemical reactions, one should know the stable conformations and parameters of potential functions of molecules. This knowledge is also important both in understanding the nature of condensed phases and the theory of polymers. There are good reasons to believe that data on conformations of small molecules could serve as a strict criteria for the present theories of molecular structure.

Physical methods of investigation are widely used in conformational analysis. One of the most effective methods is vibrational spectroscopy. Compounds with two or more stable conformations were studied using IR and Raman spectra in recent years. It is well known how to solve a number of conformational problems using these methods. Methodical aspects and data concerning this question are given in monographs [1, 2] and reviews [3, 4]. New possibilities for applying the vibrational spectroscopy in conformational analysis appeared during the recent 10–15 years due to the development of experimental equipment, and the computer treatment of the results. This review is concerned with some directions in this field which were developed during these years:

(a) Determination of the structure (conformation) of compounds by relative band dichroism in the polarized IR spectra of crystals (Part 2).

(b) Determination of the entropy differences of conformers and kinetic characteristics of the conformational transitions by IR spectra (Parts 3, 4).

(c) The possibilities of IR spectroscopy in studying the influence of medium (liquid, glassy) on the conformational equilibria and dynamics of conformational transitions (Parts 5, 6).

(d) Study of the crystallization kinetics in amorphous films containing molecules with various conformations (Part 7).

(e) Study of the hindered rotation of the methyl groups in crystals by halfwidths of IR absorption bands (Part 8).

(f) Observation of the conformational inhomogeneity in compounds by the form of the inhomogeneously broadened lines in Coherent anti-Stokes Raman Scattering spectra (Part 9).

Of course, these aspects do not limit new data which recently appeared in literature. First of all, their choice is determined by the scientific interests of the authors.

We hope that this review will be of interest to all specialists who study structure and dynamics of molecules.

The following chemical abbreviations are used:
Sulphone I—$CH_3SO_2CH_2Cl$;
Sulphone II—$CH_3SO_2CH_2Br$;